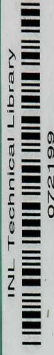


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ANNUAL REPORT ON
DWMT PROJECT ANO115A

FY 1975

by

S. M. Fried, A. M. Friedman,
J. J. Hines, and L. A. Quarterman



U.S. GOVERNMENT

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Chemistry Division

September 1975

Previous report: ANL-8115

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I. INTRODUCTION

The migration of actinide wastes, especially the long-lived isotopes of plutonium and americium, in rocks and soils, is of special interest since any major release of stored wastes from a depository will proceed by this path. It is therefore important to study the mechanisms involved in this migration.

For the sake of completeness, the previous results (FY 1974) are summarized before those of the past year are discussed.

The studies in FY 1974 led to several important conclusions. One of these was the experimental verification of the assumption that a dynamic process, such as the migration of plutonium in a solution flowing through a fissure or through pores, could be described in terms of a simple variable. The variable was found to be the surface absorption coefficient. (This coefficient, k , is defined as the ratio of activity in a milliliter of solution to the activity absorbed per square centimeter of rock.) This coefficient was measured in a static system by equilibrating solid samples of stone of known surface area with solutions of plutonium or americium in the appropriate chemical milieu. It was shown that these static coefficients and the physical constants of the system (pore size, flow, volume, etc.) were sufficient to predict the distance migrated. These coefficients were measured for various types of solutions, and it was demonstrated that they were sensitive to the concentration and types of other ions present. In general, desorption of actinide ions occurred if the aqueous phase contained high concentrations of other cations. It was evident that this year measurements should be made both of the kinetics of the equilibrium process and of the values of k in aqueous solutions containing high concentrations of salts.

One other important result of this previous study was the identification of two chemical forms of Pu(IV). One of these forms, assumed to be ionic and highly charged, migrated at a rate tenfold less rapid than the second form, assumed to be a polymer. The investigation of the rapidly migrating form was felt to be one of our highest priorities in FY 1975 and FY 1976.

In addition, the success of our computer model in the prediction of flow through fissures made it feasible to consider preparing a laboratory-scale

model of a migration experiment to test the predicted behavior of plutonium on rock samples taken from an existing waste depository.

These objectives have been achieved, and arrangements have been made with the Environmental Studies Group (H-8) at Los Alamos for a joint core-drilling program with ANL. This will be carried out at a former disposal site whose history is documented. The objective will be to acquire core samples (containing actinides) at carefully determined coordinates from the point (or points) of deposition of the actinide wastes. It is intended that the actinide concentrations be determined in such cores and the results tabulated so that the pattern of migration from a real depository can be discerned.

II. EXPERIMENTAL RESULTS

A. General Studies of Plutonium and Americium Migration

The absorption coefficients of Am(III) and Pu(IV) on solid cores of Los Alamos tuff and Idaho basalt* from aqueous solutions were measured at a pH ranging from 2 to 10. These were equilibrium studies, and it was found that after the first 24 hr k had a constant value.

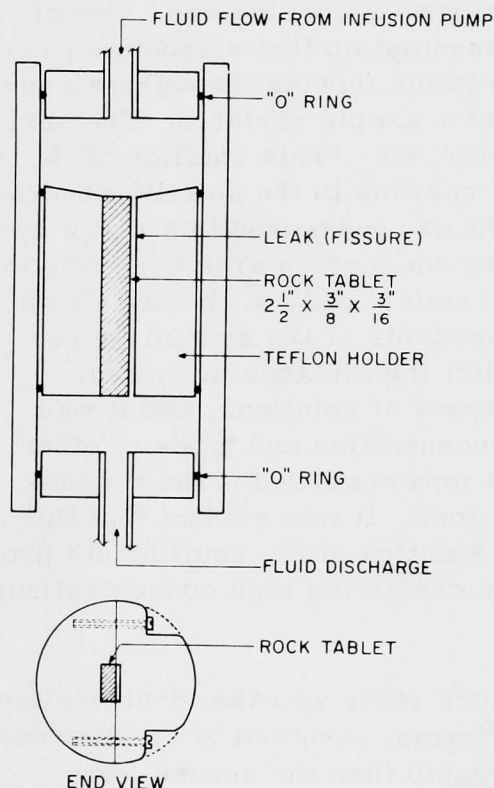


Fig. 1. Artificial-fissure Apparatus.
ANL Neg. No. 122-1309.

The movement of Pu(IV) through Idaho basalt fissures was traced with two objectives in mind. The first objective was to determine if the presence of the more rapidly migrating chemical form of plutonium was affected by the kinetics of the experiment. For example, can the two forms of plutonium exchange by a slow equilibrium? If so, a very slow flow rate along the surface of a fissure may cause the plutonium to migrate as a single slowly moving band, since the equilibrium will be shifted towards the more strongly bound form. However, a rapid flow rate will not permit equilibrium to be established; the two forms will therefore become separated, giving either two peaks or a broad peak.

The simulation of the fissure was accomplished by the apparatus shown in Fig. 1. Tablets of basalt were cut with smooth surfaces. Five of the six surfaces of the tablet were rendered impervious to water by coating them with wax. The sixth surface was left untreated and was held in the apparatus in

*The basalt was taken from the EBR(II) waste-disposal site at the Idaho National Engineering Laboratory near Idaho Falls, Idaho.

such a manner as to be exposed to and wetted by a solution containing plutonium. This "active" surface was held in the apparatus in such a way that it faced an inert surface (Teflon) a short distance away (about 0.01 cm) as shown in Fig. 1. The space between the basalt and Teflon surfaces then constituted the fissure through which the aqueous medium could flow. Since all other surfaces of the basalt were waxed, they did not participate in the experiment, and all results on the distribution of plutonium on the surface of the basalt were unperturbed by effects that would have otherwise related to more complex geometries.

The plutonium was introduced at the top of the fissure in a very small volume (about 50 λ) by means of an infusion pump. The subsequent elution of the adsorbed plutonium from the surface of the basalt also made use of the infusion pump. Water was the elution medium, and since the infusion pump was constructed to deliver steady, slow, predetermined volumes, it was well suited for this kind of experiment.

After the requisite amount of water had been allowed to flow over the surface of the basalt, it was stopped and the basalt tablet was removed from its holder and dried. Scanning the surface of the rock for alpha activity by means of a scanning alpha counter (SADSAC) delineated the distribution of the plutonium on the rock.

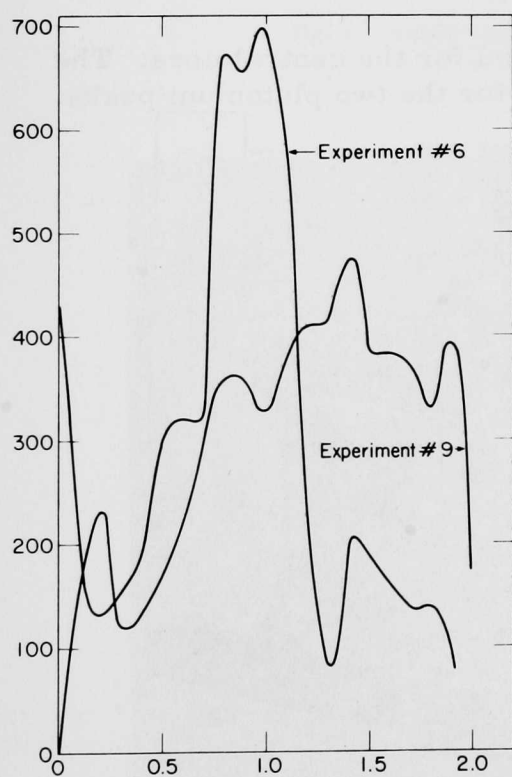


Fig. 2. Counting Rate of Plutonium (counts/min-cm²) as a Function of Distance Traveled down Fissure (cm). ANL Neg. No. 122-75-316.

Varying the delivery rate of the infusion pump, as well as the total volume of water used, made it possible to examine the distribution of plutonium as a function of these parameters. For example, the apparatus was used in a series of survey experiments to determine the effects of flow velocities. The results indicate a nonequilibrium behavior. Figure 2 is a composite plot of the results of experiments on similar slabs of basalt. The curve marked experiment 6 was taken using a flow velocity of 17.2 cm/hr; experiment 9 used 51.7 cm/hr. As can be seen, at the slower velocity the peak is much sharper.

B. Modeling Studies -- Computer Model

A computer model, based on multiple reiteration of surface absorption and dissolution processes, was developed, representing the migration process through pores and along the surfaces of fissures. The model, which uses only the physical dimensions and surface absorption coefficients for the particular system, adequately describes the

main features of the migration process. However, it does not take into account the second-order effects of nonsaturated flow and kinetic dispersion. The predictions of the model, along with the results of our laboratory modeling experiment, are discussed in the following section.

C. Modeling Studies--Laboratory-scale Model

A laboratory-scale model of the migration of plutonium was studied using a block of tuff (25 x 30 x 23 cm) from the Los Alamos site. Figure 3 shows the experimental setup. Tracer ^{237}Pu was obtained for this experiment to facilitate counting. The plutonium was delivered to the center of a 1 x 2 x 0.5-cm indentation on the surface of the block. The delivery was made by means of the infusion pump at such a slow rate that the solution dried at the delivery point with little or no spreading. To simulate rainfall, the surface was alternately wet by means of a sprinkler and then allowed to dry. A total of 1270 ml of water was delivered in six 75-300-ml doses over a seven-day period, after which the rock was allowed to dry for four days. The rock was then cored as shown in Fig. 4. A diagrammatic view of the coring apparatus is shown in Fig. 5. The results of the distribution measurements are shown in Fig. 6 for cores taken at various radial distances from the central deposit of plutonium. Figure 7 is a cross-sectional view of the distribution obtained. It is easily seen that there are two plutonium concentration peaks, presumably corresponding to the ionic and hydrolyzed forms.

Figure 8 shows the distribution observed for the central core. The dotted lines show the computer-model results for the two plutonium peaks.

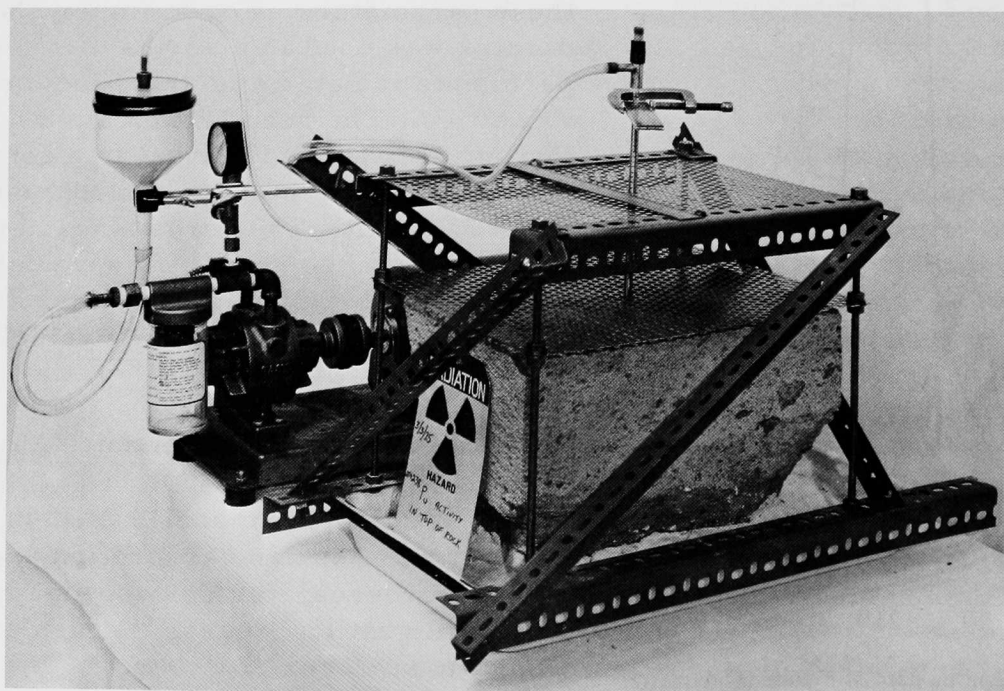


Fig. 3. Experimental Arrangement for Coring Experiment. ANL Neg. No. 122-2443.

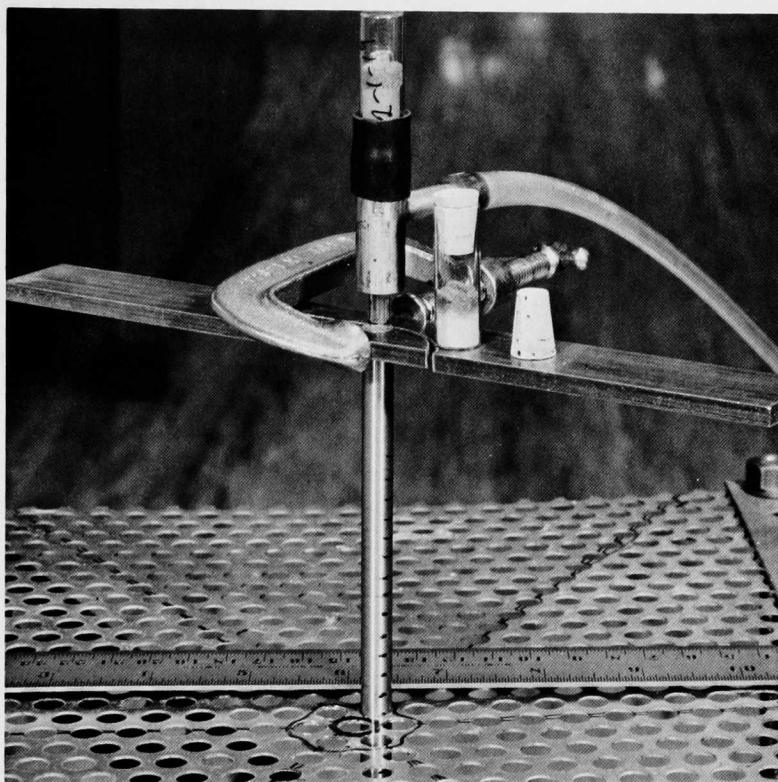


Fig. 4. Sample-coring Apparatus. ANL Neg. No. 122-2406.

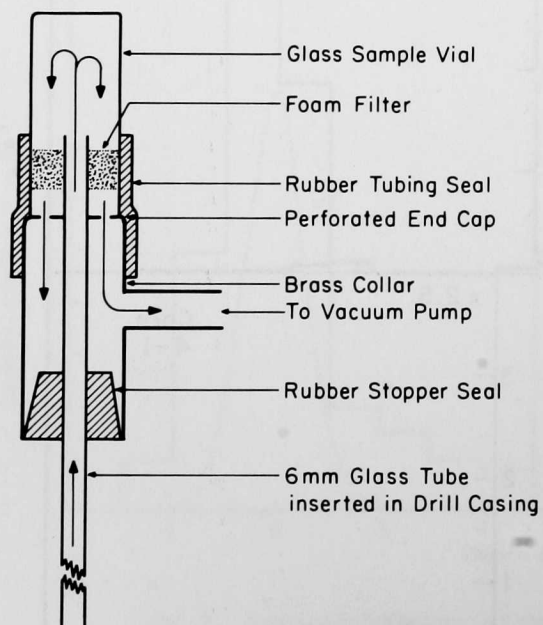


Fig. 5

Schematic Diagram of Coring Apparatus. ANL Neg. No. 122-75-105.

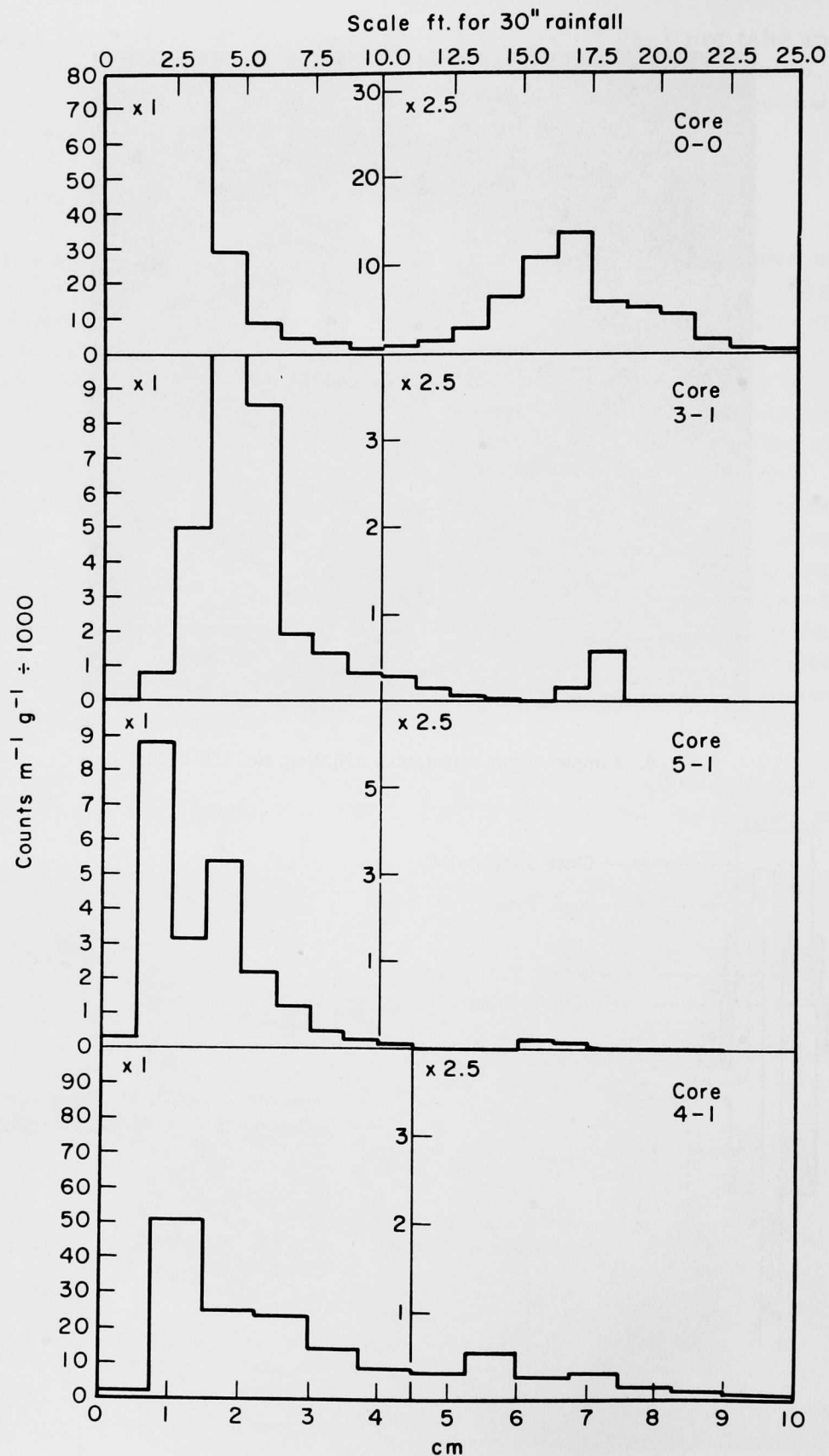


Fig. 6. Results for Cores Taken at Various Radial Distances from Central Core (0-0). ANL Neg. No. 122-75-104.

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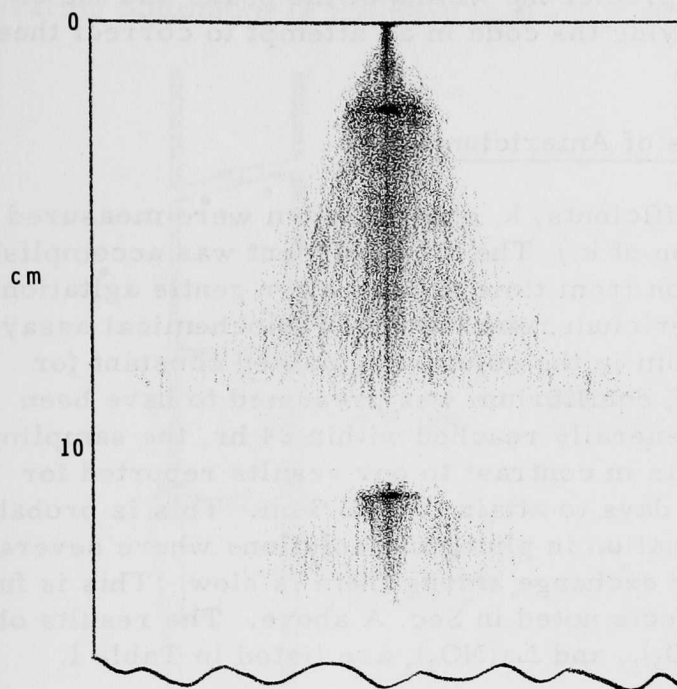


Fig. 7

Cross-sectional View of Activity Distribution. ANL Neg. No. 122-75-107 Rev. 1.

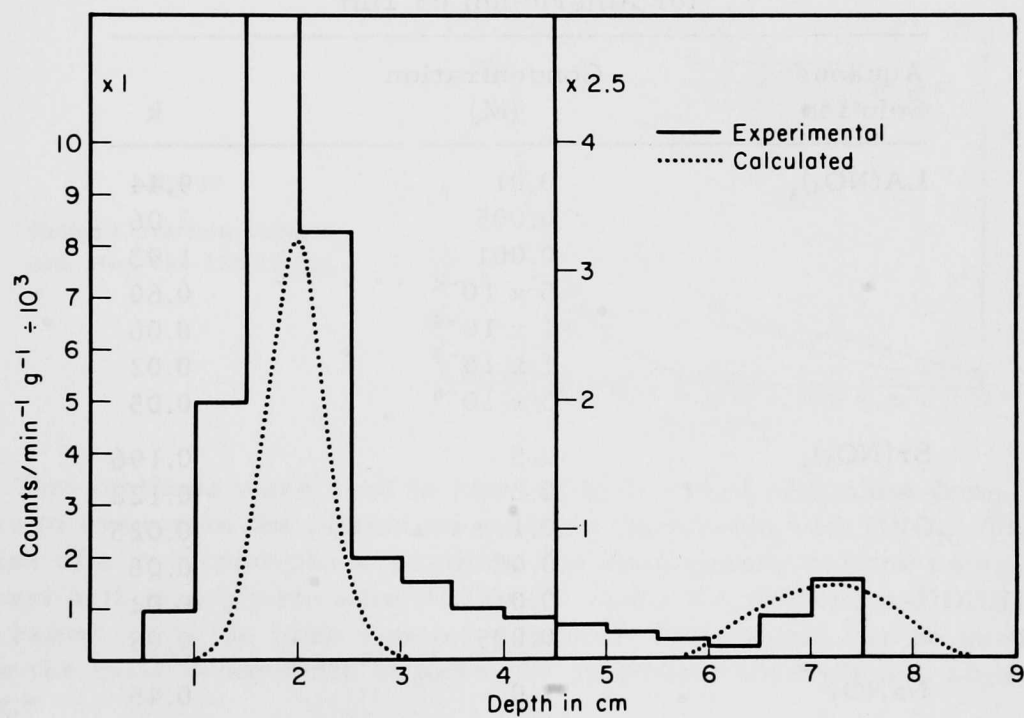


Fig. 8. Activity Distribution in Central Core; Dotted Line is Result of Model Calculation. ANL Neg. No. 122-75-106.

As can be seen, the model fails to predict the widths of the peaks and the exponential gradients. We are modifying the code in an attempt to correct these discrepancies.

D. Surface Absorption Coefficients of Americium

The surface absorption coefficients, k , of americium were measured for basalt. (See Sec. I for definition of k .) The measurement was accomplished by sampling the supernatant solution from time to time after gentle agitation and determining the amount of americium remaining by radiochemical assay. When the concentration of americium in the solution remained constant for several successive determinations, equilibrium was presumed to have been attained. While equilibrium was generally reached within 24 hr, the sampling was continued for five days. This is in contrast to our results reported for plutonium, which required several days to attain equilibrium. This is probably indicative of the more complex situation in plutonium solutions where several species of ions are present and the exchange among them is slow. This is further confirmation of the kinetic effects noted in Sec. A above. The results obtained in solutions of NaNO_3 , $\text{Sr}(\text{NO}_3)_2$, and $\text{La}(\text{NO}_3)_3$ are listed in Table I.

TABLE I. Surface Absorption Coefficients
for Americium on Tuff

Aqueous Solution	Concentration (M)	k
$\text{La}(\text{NO}_3)_3$	0.01	9.44
	0.005	3.06
	0.001	1.93
	5×10^{-4}	0.60
	1×10^{-4}	0.06
	1×10^{-5}	0.02
	5×10^{-6}	0.05
$\text{Sr}(\text{NO}_3)_2$	0.5	0.196
	0.2	0.122
	0.1	0.025
	0.05	0.06
	0.01	0.02
	0.005	0.08
NaNO_3	1.0	0.45
	0.5	1.50
	0.1	0.013
	0.05	0.16

E. Chemical Identification of the Rapidly Migrating Form of Plutonium

Eluting plutonium solutions through columns made of plugs of tuff, as shown in Fig. 9, has been shown to separate the two forms of plutonium. This

typical elution curve can be seen in Fig. 10 as a solid curve. The rapid migrating plutonium is the peak at the left of the figure.

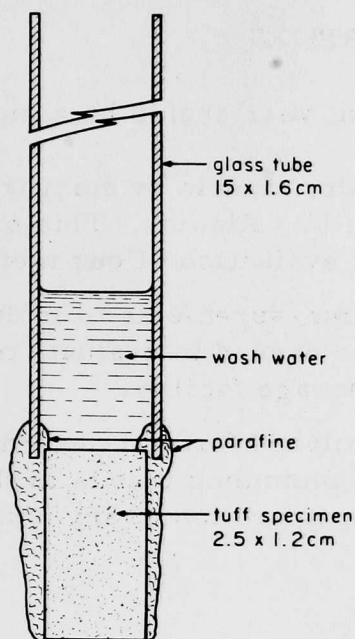


Fig. 9

Schematic Diagram of Elution Column Made with a Plug of Tuff. ANL Neg. No. 122-75-103.

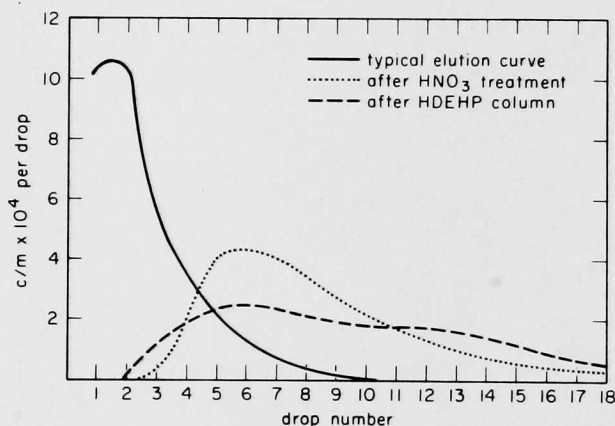


Fig. 10

Elution Curves from Column.
ANL Neg. No. 122-75-108.

Two methods were used to remove hydrolyzed plutonium from solution. One was to evaporate the plutonium solution repeatedly with HNO_3 . The other made use of a reversed-phase partition chromatography column using di-2-ethylhexyl orthophosphoric acid (HDEHP). Since the plutonium-HDEHP system is well known (only the ionic species adsorbs), this column can be used to determine the relative amounts of ionic and polymeric (hydrolyzed) plutonium present.*

When plutonium from recently evaporated HNO_3 solutions was used, the rapidly migrating plutonium peak did not appear. The same result was obtained by removing the polymeric species with an HDEHP column and using only the adsorbed ionic material as feed.

*Dr. E. P. Horwitz of this laboratory kindly supplied us with an HDEHP column.

Both of the above results are also shown in Fig. 10.

III. FUTURE PRIORITIES

We feel that our program in the current year should be aimed at:

1. Testing our computer and laboratory models by comparison with results obtained at the plutonium waste site in Los Alamos. This onsite test under field conditions will provide a stringent evaluation of our method.
2. Extending our surface absorption measurements to include concentrated salt solutions. These results will be needed to evaluate migration in case of water entrance into a bedded salt storage facility.
3. Studying the formation of the hydrolyzed form of plutonium and investigating ways of minimizing the fraction of plutonium that is in this form. This minimization is obviously pertinent to the operation of any plutonium storage facility.

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